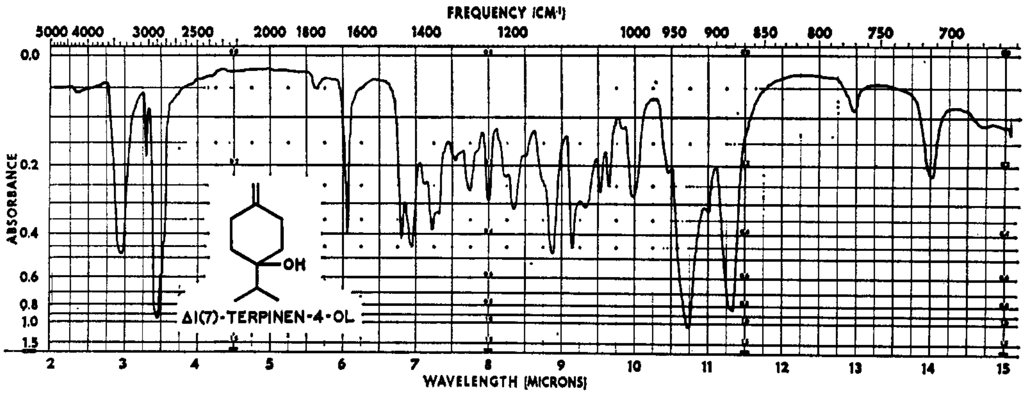

Figure 1.

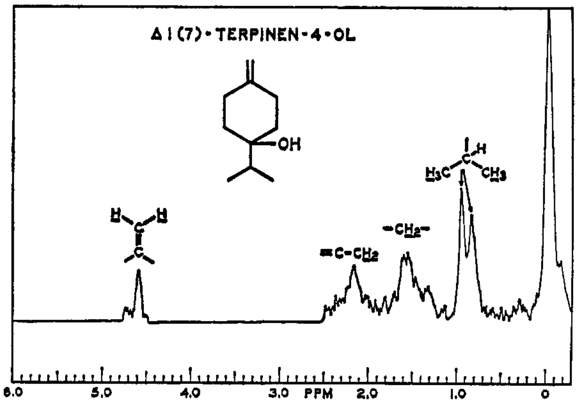

Figure 2.

Experimental Section

Approximately 7 g of 1(7),4(8)-*p*-methadiene was prepared as previously described.[2] This was placed into a 250-ml reaction flask equipped with a stirrer, thermometer, reflux condenser, dropping funnel, and Dry Ice bath. Anhydrous sodium acetate (8.2 g) and 40 ml of methylene chloride were added. The mixture was cooled to 0° and 10 g of 40% peracetic acid was added at 0-5° over a period of 2 hr. Stirring was continued at 0-5° for 3 hr. Water (30 ml) was added to the reaction mixture, and stirring was continued for 1 hr. The organic layer was washed with sodium bicarbonate and salt solutions and dried; the solvent was evaporated. The resulting 8 g of oil was then added (over a period of 1.25 hr) to 38 g of lithium aluminum hydride in 38 g of tetrahydrofuran in a 250-ml reaction flask, equipped with a stirrer, thermometer, reflux condenser, nitrogen purge, dropping funnel, and heating mantle.

The reaction mixture was then heated at reflux for 3 hr and cooled to 0-5°, and 20 ml of H_2O was added over a 1-hr period.

The product, isolated by extraction and solvent recovery, was passed through a preparative gas chromatograph which consisted of a 10 ft × $^3/_8$ in. o.d. column containing 20% Carbowax 20M on silane-treated Celite at 150° with a helium flow rate of 250 cc/min. Successive 100-mg injections were made until 400 mg of 1(7)-terpinen-4-ol was obtained. Approximately 100 mg of δ terpinenol was also obtained which elutes after the 1(7)-terpinen-4-ol.

The product was then passed through a preparative gas chromatograph which consisted of a 10 ft × 0.25 in. o.d. column containing 20% Se-30 on 60-80 mesh silane-treated Chromosorb W, at 125° with a helium flow rate of 100 cc/min. Repeated 10-μl injections were employed and 200 mg of very pure product was thus obtained.

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The Shielding Effect of the Nitro Group

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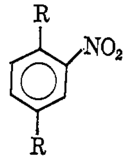
In recent years, the long-range shielding effect of the nitro group has been observed in *t*-butylnitrocyclohexanes,[1] nitrotestosterones,[2] nitrocholestenes,[3] nitroporphyrins,[4] nitronaphthalenes,[5] and nitromethylbenzenes.[6] We have examined the nmr spectra of the 2-nitro derivatives of *p*-xylene (**2**) and of the *p*-diethyl- (**3**), *p*-diisopropyl- (**4**), and *p*-di-*t*-butylbenzenes (**5**).



1, R = H
2, R = CH_3
3, R = CH_2CH_3
4, R = $CH(CH_3)_2$
5, R = $C(CH_3)_3$

In Table I there is presented the difference in chemical shift (downfield) (determined in two inert solvents) of the *ortho* proton in the nitro compound relative to the corresponding proton in the parent hydrocarbon. Also presented is the degree of twist φ of the nitro group from coplanarity with the aromatic ring as calculated by Wepster[7] from ultraviolet data. The corresponding shift difference of the *meta* and *para* protons is also tabulated. The observed signals in the nitro compounds are broad singlets (two unre-

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solved regions which should be the AB and X portions of an ABX spectrum).

Table I

Shift Differences of Ring Protons

Compd	Δppm, CCl_4	*ortho*, cyclohexane	φ, deg, isooctane	Δppm, CCl_4	*meta, para*,[a] cyclohexane
1[b]	. . .	0.95	0	. . .	0.21 *meta*, 0.33 *para*
2	0.75	0.72	34	0.25	0.18
3	0.63	0.63	40	0.23	0.18
4	0.42	0.45	47	0.30	0.27
5	−0.02	0.00	65	0.18	0.13

[a] Except for **1**, the *meta* and *para* shifts were not resolved and are recorded as one peak. [b] Data of H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 721 (1961).

In Table II there is recorded the difference in chemical shifts of the *o*- and *m*-benzylic protons relative to the corresponding protons in the parent hydrocarbons. The values were determined in CCl_4 because the cyclohexane resonance interfered with the determination in that solvent.

Table II

Shift Differences of Benzylic Protons

Compd	Δppm, *o*-benzylic	Δppm, *m*-benzylic
2	0.25	0.13
3	0.30	0.13
4	0.55	0.12

The data in Table I concerning the *ortho* proton shifts can be evaluated if two reasonable assumptions are made. First, since the *meta,para* resonance is relatively constant through the series, these protons serve as internal standards that demonstrate that change of ring anisotropy, ring electron density, dipole moment, etc., does not make the major contribution to change in *ortho* shift as a function of nitro twist. Second, we assume that in nitrobenzene, a large part of the deshielding of the *ortho* proton, in the light of previous work, can be attributed to anisotropic deshielding. Then, the decrease in deshielding in nitroxylene, as the nitro group is twisted 34° out of the plane, can be explained by suggesting that the *ortho* proton is no longer in the center of the deshielding region. The increasing deviation of the nitro group from coplanarity with the ring in the ethyl and isopropyl cases further removes the *ortho* proton from the region of maximum deshielding and the chemical shift difference decreases in a consistent manner. Finally, in the *t*-butyl case, the nitro group has twisted far enough so that its *shielding* region now affects the *ortho* proton, the signal of which is at higher field than the *meta* and *para* proton signal. The interesting datum in Table II is the seemingly disproportionate deshielding of the *o*-benzylic proton in the isopropyl system. The shift is explained by postulating the existence of a preferred (and model-justified) rotamer of the isopropyl group that keeps the methyl groups away from the nitro group. The benzylic hydrogen is then in the plane of the benzene ring and always subject to the large anisotropic deshielding arising out of the ring current. In the parent compound, the proton is in a freely rotating system and is not maximally deshielded. The experiment testing this hypothesis, that is, obtaining spectra at 70 and 150°, showed no significant shift of the *o*-benzylic proton signal (relative to the other signals). Therefore, the barrier to free rotation of the isopropyl group is very high.

The entire chemical shift of the *ortho* proton in the nitroaromatics relative to the hydrocarbons is not only due to anisotropic effects. Our data has been subjected to some calculations. Attempts were made to separate out the nonanisotropic contributions based on the correlation of inductive and resonance parameters with chemical shift[8] and on an electric field hypothesis.[9] The derived numbers were used to evaluate magnetic susceptibilities.[10] However, these calculations are of dubious merit because the separation of effects at *ortho* positions is speculative, and the theory for the evaluation of magnetic susceptibilities is not valid at small distances.

Experimental Section

The *p*-xylene, 2-nitro-1,4-dimethylbenzene (**2**), and *p*-diisopropylbenzene were commercial samples used without further purification. A sample of *p*-diethylbenzene, bp 184°, was prepared by Wolff–Kishner reduction[11] of the semicarbazone of *p*-ethylacetophenone, mp 188–191° (lit. 191°).[12] Nitration of the hydrocarbon according to a published procedure afforded 2-nitro 1,4-diethylbenzene (**3**), bp 100–103° (1 mm) [lit. 137–140° (12 mm)].[13] A small sample obtained by subsequent chromatography on silica (Davison) was used for nmr analysis. Fractional distillation of the nitration product of *p*-diisopropylbenzene did not yield pure 2-nitro-1,4-diisopropylbenzene (**4**) as had been reported.[14] A fraction, bp 152–158° (25 mm), was chromatographed on silica (Davison) and yielded a homogeneous product. The *p*-di-*t*-butylbenzene, mp 77° (lit. 77–79°),[15] and its nitro derivative (**5**), mp 89–90° (lit. 75–78°),[15] were prepared according to published procedures. The nitro derivative formed solid solutions with the hydrocarbon and the high-melting product was obtained by chromatography on silica.

The nmr spectra were determined with a Varian A-60 instrument using 10% (by weight) solutions in CCl_4 and 7% solutions in cyclohexane. Tetramethylsilane was the internal reference in the first solvent and the solvent absorption itself was used in

Table III

Shifts of Hydrocarbons

Compd	Ring		Benzylic	Other
	CCl_4	Cyclohexane	CCl_4	CCl_4
Xylene	416	330	135	
Diethylbenzene	419	333	154[a]	72[b]
Diisopropylbenzene	422	335	169[c]	74[d]
Di-*t*-butylbenzene	433	347		76

[a] Quartet, $J = 7$ cps. [b] Triplet, $J = 7$ cps. [c] Heptet, $J = 7$ cps. [d] Doublet, $J = 7$ cps.

Table IV

Shifts of Nitro Compounds

Compd	Ring *ortho*		Ring *meta, para*		Benzylic CCl_4		Other
	CCl_4	Cyclohexane	CCl_4	Cyclohexane	*ortho*	*meta*	CCl_4
2	461	373	431	341	150	143	
3	457	371	433	344	172[a]	162[a]	76[b]
4	447	362	440	351	202[c]	176[c]	77[d]
5	432	347	444	355			77, 82

[a] Overlapping quartets. [b] Distorted triplet. [c] Overlapping heptets. [d] Distorted doublet.

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the second case. The raw nmr data is assembled in two tables. Table III records proton signals for the hydrocarbons in cycles per second relative to the internal reference. Table IV records the signals for the nitro derivatives.

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Chlorosulfonation of Triphenyl Phosphate, Diphenyl Methylphosphonate, and Triphenylphosphine Oxide

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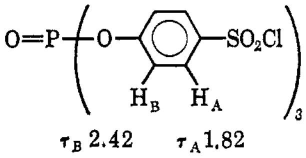
Reports of substitution reactions on aryl groups either attached directly to phosphorus or through carbon as in tertiary phosphine oxides are quite meager. The majority of such reactions have been confined to nitration of the aryl substituent.[1] Stachlewska-Wroblowa and Okon[2] have, in addition to nitration, investigated the sulfonation and chlorosulfonation of triphenylphosphine oxide and its derivatives. The chlorosulfonation of 4-methoxyphenylphosphonic acid to yield 3-chlorosulfonyl-4-methoxyphenylphosphonic acid was also reported in a patent.[3]

Of particular interest to us was the chlorosulfonation of triphenylphosphine oxide and the possible extension of the chlorosulfonation reaction to neutral pentavalent phosphorus esters containing at least one aryl group. The subject of electrophilic substitution reactions involving such phosphorus esters has received even less attention than that afforded tertiary phosphine oxides. In both cases substitution on the pendant aryl group is most often effected prior to formation of the phosphorus ester or phosphine oxide. This is usually desirable especially in the case of the somewhat labile phosphorus esters. In view of this lability, the stability of aryloxy phosphorus bonds, particularly toward chlorosulfonic acid and the attending conditions, was somewhat questionable.

Subsequently, it was found that triphenyl phosphate can be chlorosulfonated readily with apparently little deleterious effect on the aryloxy phosphorus bond. Addition of the phosphate to excess chlorosulfonic acid at room temperature caused a readily controlled exotherm, and hydrogen chloride was evolved. Moderate heating of the reaction mixture, until hydrogen chloride evolution subsided, followed by conventional work-up, yielded chlorosulfonated triphenyl phosphate. The reaction product was identified by elemental analysis, molecular weight determination, and infrared and pmr spectra as tris(*p*-chlorosulfonylphenyl) phosphate (1). The reaction conditions were not optimized. However, variation of the molar ratio of reactants, while maintaining reaction time and temperature constant, indicated that a 30:1 mole ratio of chlorosulfonic acid to phosphate reacted at 50° for 6 hr afforded high yields (>80%) of crude 1. The reaction was repeated several times using these conditions with comparable results. When chlorosulfonic acid and triphenyl phosphate were allowed to react at molar ratios of 24:1, 18:1, and 12:1, the yields of crude chlorosulfonated phosphate (1) were 77, 73, and 54%, respectively. Reported[4] methods for reducing the amount of excess chlorosulfonic acid, such as the utilization of sodium chloride, alone or in combination with inert organic solvents (*e.g.*, carbon tetrachloride), were not investigated.

The chlorosulfonation of diphenyl methylphosphonate was also found to proceed readily, utilizing reaction conditions that produced high yields of chlorosulfonated triphenyl phosphate (1) and a mole ratio of chlorosulfonic acid to phosphonate of 20:1. The reaction product identified as bis(*p*-chlorosulfonylphenyl) methylphosphonate (2) by elemental analysis, molecular weight determination, and infrared and pmr spectra was obtained in better than 79% crude yield.

That chlorosulfonation of triphenyl phosphate and diphenyl methylphosphonate occurs predominately at the *para* position was demonstrated by the infrared and pmr spectra of the reaction products. *para* substitution of both the chlorosulfonated phosphate (1) and phosphonate (2) was manifested by characteristic infrared absorption in the regions 6.3–7.2 μ and 11.5–12.5 μ. The pmr spectrum of 1 in $CDCl_3$ (TMS as internal reference) exhibited the characteristic AB quartet of a *para*-substituted benzene (τ_A 1.82, τ_B 2.42 ppm; J_{AB} = 8.7 cps). The chlorosulfonated phosphonate (2) in $CDCl_3$ showed the expected methyl doublet (τ = 8.02 ppm,[2] J_{PH} = *ca.* 18 cps) for $P-CH_3$ and the characteristic AB pattern of a *para*-substituted benzene (τ_A = 1.90, τ_B = 2.51 ppm; J_{AB} = 8.7 cps). In both 1 and 2, a long-range coupling of phosphorus to H_B ($^4J_{PH}$ = 1.0 cps) was observed and provided further support for the assigned structures. Similar four-bond couplings have been observed in a number of other organophosphorus compounds.[5] In neither case was there any evidence for the presence of other isomers in amounts greater than *ca.* 5%. In the case of the



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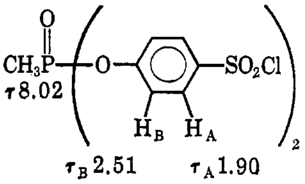

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